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Strong-field ionization of water by intense few-cycle laser pulses

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Ionization of H_2O is caused by four-cycle pulses of intense 800-nm light in the temporal regime where processes like enhanced ionization and spatial alignment are "switched off" and recollision dominates the laser-molecule interaction. Nonadiabatic effects drive the overall dynamics in the few-cycle regime and give rise to multiple ionization of the molecule to electronically excited ionic states. The direct experimental manifestation of such nonadiabatic effects is in significantly higher amounts of kinetic energy being released upon dissociation into atomic fragments. The energy spectrum of H^+ fragments enables us to deduce that recollision of the optical-field-ejected electron with the molecular ion drives the overall dynamics.

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I. INTRODUCTION

The ready availability of intense optical fields that are generated by means of femtosecond lasers has resulted in considerable and widespread contemporary interest in studies of molecular dynamics in the strong-field regime, in which the magnitude of the light field becomes comparable to the intramolecular Coulombic field (for a recent compilation of cogent reviews, see [1] and references therein). In such circumstances, the overall laser-molecule interaction is dominated by single and multiple ionization and the consequent rupturing of one or several bonds. Most experimental studies of strong-field molecular dynamics have hitherto relied on the measurement of ion yields made with pulses of infrared light that are several tens to several hundred femtoseconds long. It seems well established that three processes constitute the main drivers of molecular dynamics in strong fields—enhanced ionization (EI), spatial alignment, and recollision ionization—and a considerable body of work that has been carried out in the course of the last few years has succeeded in obtaining insights into the relative importance of these processes in different intensity and temporal regimes [1]. Very recently, several laboratories have begun to gain access to methods that enable ultrashort pulses of light to be generated, with pulse durations short enough to ensure that only a handful of optical cycles constitute a single pulse. Might the use of few-cycle pulses result in new insights into strong-field molecular dynamics? This question constitutes the main motivation for us to study strong-field ionization and dissociation of isolated water molecules using four-cycle pulses of 800-nm light.

Experiments on molecules subjected to intense, ultrashort laser pulses have been reported [2] that offer indications that dynamic spatial alignment of molecules like O_2 and N_2 does not occur in the few-cycle regime: the duration of the optical field in this ultrashort regime is far too short for polarization-induced torque to act on the N-N or O-O axis. Moreover, the process of enhanced ionization is also expected to be effectively "switched off" in such studies as there is insufficient time for the bond length in molecules to elongate to the critical distance at which ionization propensity is enhanced [3]. Consequently, it is not unreasonable to expect that strong-field dynamics in the few-cycle regime might be essentially driven by one process, recollisions, wherein the ionized electron oscillates in the optical field and recollides with the molecular ion, inducing further ionization. Few-cycle pulses, therefore, offer to molecular physicists tantalizing prospects of, on the one hand, being able to disentangle effects of different processes in strong-field molecular dynamics and, on the other, of possibly being able to exercise some measure of control on the overall dynamics by tuning the intensity and duration of the ultrashort optical field. Indications of the former have been presented by us recently [4], while the possibility of the latter has been indicated by results on few-cycle ionization of hydrogen molecules [5]. Hydrogen migration in methanol molecules following strong-field double ionization has also been recently studied [6], and differences have been discerned in the Coulomb explosion dynamics that seem to depend on whether methanol is irradiated by 7-fs pulses or 21-fs pulses. Although linear chains of hydrocarbon molecules have been studied with 40-fs pulses by Lezius and co-workers [7], there is sparse systematic information on the fragmentation of small molecules in the ultrashort regime. Experiments on dissociative ionization of methane have indicated the importance of nonadiabatic effects in that the propensity for molecular ionization in strong fields of a few tens of femtoseconds duration is enhanced compared to the situation that prevails when longer-duration fields are used [8].

In the work that we report here, our experimental handle on adiabaticity is the laser pulse duration. We note that experiments conducted using laser pulses of ~100 fs duration or so allow access to the temporal regime in which changes in field amplitude are relatively small between successive optical cycles. This implies an adiabaticity in the electron dynamics: on reaching the field strength required for tunnel ionization, the electron escapes before there is any further increase in field strength. However, the electronic response is no longer adiabatic for pulses of 10 fs duration: the ionized electron is then exposed to much higher, rapidly increasing field strengths, thereby gaining more energy before recollision occurs. Indeed, in experiments on high harmonic gen-

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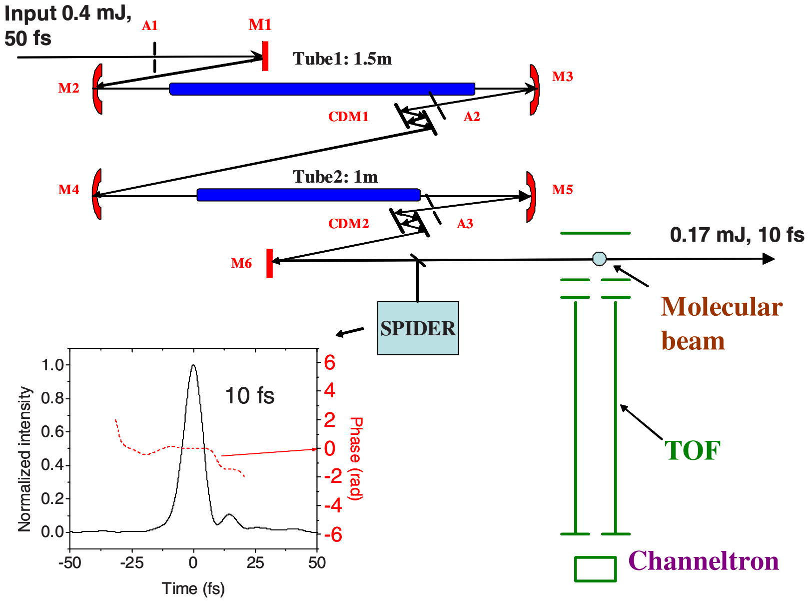

FIG. 1. (Color online) Schematic depiction of the experimental apparatus. The 10-fs pulses were generated using two Ar-filled tubes (tube 1 and tube 2) in tandem. The white light resulting from the tubes was recompressed using sets of chirped dielectric mirrors (CDM1 and CDM2), and diagnosis of the compressed pulses was by means of SPIDER (see text). A typical SPIDER trace showing 10-fs pulses is illustrated, with the measured phase information in red. *A*1–*A*3 are apertures; *M*1–*M*6 are metallic mirrors. TOF denotes a 20-cm-long linear time-of-flight spectrometer.

eration (HHG) in Ar [9,10], the spectrum obtained with 25-fs pulses contains harmonics that are many orders higher than when 100-fs pulses of the same intensity are used, a direct consequence of the atom surviving to higher laser intensities. A cogent overview of atomic dynamics in ultrashort optical fields has been provided by Brabec and Krausz [11].

But how might a molecule respond to nonadiabaticity in strong-field electron dynamics? This is the pertinent question that drives the present study. We note that the recollision process in polyatomic molecules [12] irradiated by 100-fs-long pulses has been shown to depend on molecular structure [13]. In the following we present results of experiments on the ionization dynamics of H_2O molecules induced by intense few-cycle (10-fs) pulses of infrared light centered around 800 nm. We focus attention on the dissociation channel that leads to formation of proton fragments. Specifically, we make detailed measurements on the kinetic energy that is released upon optical field-induced bond cleavage in the water molecule that leads to H^+ formation and show that significant differences occur in the proton kinetic energy spectra that are measured using 10-fs pulses and those measured using longer pulse durations (~100 fs). We attribute these differences to nonadiabatic effects in the ultrafast regime which give rise to multiple ionization of the molecule to electronically excited states that dissociate with larger releases of kinetic energy.

II. EXPERIMENTAL METHOD

Almost all of the small volume of work that has been reported on few-cycle ionization dynamics has been carried out using the hollow-fiber pulse (HFP) compression technique of generating ultrashort laser pulses [14]. Very recently, an alternative method of efficiently generating few-cycle pulses has also been invoked in which use is made of the process of filamentation in gas-filled tubes [15]. It is a dual-tube version of the filamentation technique that we have adopted in the present work [16], akin to what has recently been used by Guanalini *et al.* [17]. Figure 1 presents a schematic depiction of the essential features of our experimental apparatus. Instead of a single gas-filled tube within which filamentation is made to occur, we have made use of two gas tubes in tandem. Specifically, we used in the experiments that we report here 0.4-mJ 50-fs laser pulses (1-kHz repetition rate) centered at 800 nm wavelength that were obtained from a chirped pulse amplification laser system comprising a Ti-sapphire oscillator coupled to a multipass amplifier. After passing through an aperture the laser beam was focused with a metal-coated spherical mirror ($f=1$ m) onto a 1.5-m-long tube containing pure Ar at 1.2 atm pressure. The central part of the resulting broadband light was compressed by a set of chirped dielectric mirrors (CDM1) to produce 15-fs pulses (typically of 0.24 mJ energy). These pulses were then passed through another aperture and focused on to a second 1-m-long tube (filled with pure Ar at a pressure of 0.9 atm). The broadband light was compressed once again (using CDM2) to yield 10-fs (just under four-cycle) pulses with typical energy of 0.2 mJ.

We note an important advantage of the dual tandem-cell method that we adopt here is that intensity clamping in the filaments results in a significant reduction in energy fluctuations in the laser beam [16]. Such stability enhancement is, of course, of utmost importance in studies involving molecules.

We characterized our four-cycle light pulses by means of spectral phase interferometry for direct electric field reconstruction (SPIDER), and a typical experimental trace is shown in Fig. 1. Note the constant zero phase over the 10 fs pulse duration that we obtain. Our few-cycle pulses were directed through a 300-μm fused silica window into an ultrahigh-vacuum (UHV) chamber capable of being pumped down in an oil-free environment to pressures in the low-10^{-9}-Torr range, with the laser-H_2O interaction typically occurring at operating pressures of $\sim 10^{-8}$ Torr. The four-cycle pulses were precompensated for chirp and were focused within the UHV chamber by a spherical mirror ($f=5$ cm). Ion analysis was by conventional linear time-of-

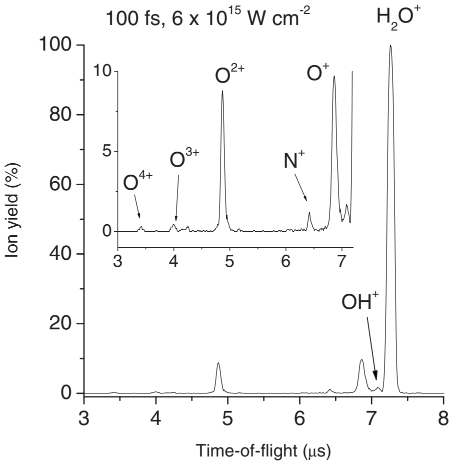

FIG. 2. Typical TOF spectrum of H_2O measured at an intensity of 6×10^{15} W cm^{-2} with 100-fs pulses of 800-nm light. The laser light was linearly polarized and aligned along the axis of the TOF spectrometer.

flight (TOF) methods, but care was taken to ensure that, by judicious use of apertures in the entrance to the TOF tube, only ions from the central most-intense portion of the laser focal volume were efficiently extracted into our spectrometer. Nearly unit extraction efficiency was ensured by use of ion extraction fields of ~100–200 V cm^{-1}; normalization of all spectra to the parent H_2O^+ peak enables ready comparison to be made of ion yields obtained under slightly different ion extraction conditions.

III. RESULTS AND DISCUSSION

The focus of our experiments is on the energy spectrum of H^+ fragments that result from dissociation of water molecules as they become singly and multiply ionized in four-cycle and longer-duration optical fields. Before considering energy spectra that we have measured, it is instructive to first present an overview of the ionization patterns that we measured in the two temporal regimes of interest in this work. Figures 2 and 3 present typical mass spectra measured at 100 fs and 10 fs, respectively, using linearly polarized laser light over the intensity range $(2-6)\times10^{15}$ W cm^{-2}. In both instances the polarization direction was along the axis of our TOF spectrometer. We took much care to ensure that the number densities of water molecules in the laser-molecule interaction zone in both sets of measurements were low enough to ensure that saturation effects were of no consequence. The spectra have been normalized with respect to the H_2O^+ peak. Major differences in the two spectra are immediately obvious. The 100-fs spectrum (Fig. 2) is dominated by the H_2O^+ molecular ion, and fragment oxygen ions, up to charge state 4+, are observed at yield levels of around 1%–10% with respect to the molecular peak. The H^+ channel is considered in more detail later. In the spectrum measured with 10-fs pulses (Fig. 3), the H_2O^+ molecular ion still dominates, but to a very much larger extent. Fragment ions are hardly observed: OH^+ and H^+ peaks correspond to yield levels around 1%, and there is no sign of multiply charged oxygen fragments at all. O^+ fragments were visible only at intensity levels of 5×10^{15} W cm^{-2} and higher. The domination of molecular ionization over fragmentation is certainly remarkable in the case of four-cycle pulses and constitutes a major difference in the overall strong-field dynamics that occur in the 10-fs and 100-fs domains.

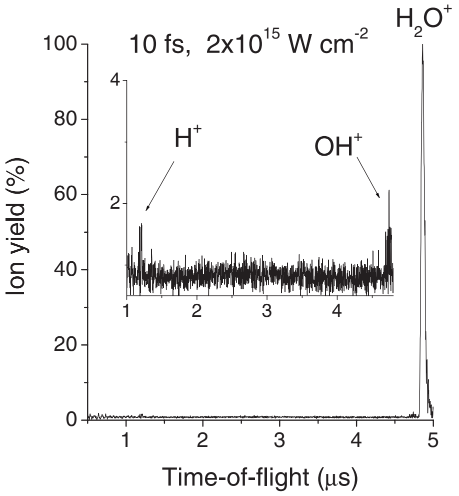

FIG. 3. Typical TOF spectrum of H_2O measured at an intensity of 2×10^{15} W cm^{-2} with 10-fs pulses of 800-nm light. The laser light was linearly polarized and aligned along the axis of the TOF spectrometer. Almost identical spectra were obtained over the range of intensities $(1-8)\times10^{15}$ W cm^{-2}. Even at the highest end of this range, typical yields of H^+ fragments did not exceed ~2%.

We now turn our attention to H^+ fragments. Typical TOF spectra that show these fragment ions are depicted in Figs. 4 and 5 for 100 fs and 10 fs, respectively. In the case of the longer-duration (100-fs) pulses, the overall morphology of our TOF spectrum is reminiscent of proton spectra obtained upon strong-field ionization of H_2 molecules (see, for example, recent measurements reported by Saugout *et al.* [18] using 40-fs pulses). This is not surprising in view of the fact that the outermost $1b_1$ orbital of H_2O is nonbonding in character, with the electron density in the molecule's ground electronic state being overwhelmingly localized around the central oxygen atom. The forward- and backward-scattered H^+ peaks that are clearly visible in the spectrum shown in Fig. 4 indicate that H^+ formation is accompanied by substantial amounts of kinetic energy. Figure 5 shows the corresponding spectrum obtained when 10-fs pulses of the same intensity were used, and again the large amount of kinetic energy accompanying H^+ fragments manifests itself very clearly in the spectrum. The double-peak feature of the H^+ ion spectra in both Figs. 4 and 5 indicates that the fragmentation is highly directional. Indeed, measurements that we made using laser polarization that is perpendicular to our spectrometer axis (data not shown) yielded a broad unstructured peak in both temporal domains. The typical value of kinetic energy associated with such a peak was determined by us to be ~350 meV.

It is known that a normal unimolecular fragmentation process would give rise to isotropic emission of H^+ ions [19]. In our experiments, water molecules are initially randomly oriented in space and, in the case of 10-fs-long laser pulses,

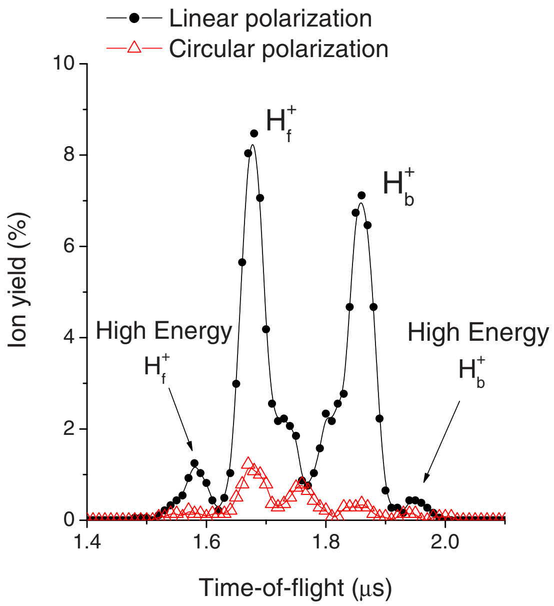

FIG. 4. (Color online) High-resolution TOF spectrum showing H^+ fragments obtained upon irradiation of H_2O with 100-fs pulses of intensity 6×10^{15} W cm^{-2}. The spectrum has been normalized to the H_2O^+ peak. Note the split peaks corresponding to low-energy, medium-energy, and high-energy protons. The subscripts *f* and *b* refer, respectively, to H^+ ions ejected towards and away from the detector placed at the end of the TOF spectrometer. The spectrum shown in red (open circles) denotes data obtained under identical optical field magnitudes, but with circularly polarized laser light (see text).

there is not sufficient time for spatial alignment to occur due to a strong enough dipole being induced in the molecule by the optical field. The ionization dynamics that gives rise to the double-peak structure must, therefore, be sensitive to one of the O-H bonds in water being aligned along the laser polarization vector. The double-peak structure is, therefore, a consequence of what is termed as geometric, rather than dynamic, alignment effects [20].

The differences in the morphology of the two sets of spectra shown in Figs. 4 and 5 indicate that although large amounts of kinetic energy are released in both cases, the shape of the 10-fs spectrum is such that higher-energy protons are obtained in the few-cycle domain. This is most clearly borne out when a simple transformation is carried out so that the time axes in Figs. 4 and 5 are mapped onto the kinetic energy. The resulting kinetic energy spectra are shown in Fig. 6. It is clear that in the case of 100-fs pulses the bulk of the H^+ fragments possess kinetic energies of ~1.5 eV, with the tail of the distribution extending to 7 eV. The spectrum obtained with 10-fs pulses indicates the formation of much "hotter" protons, with the tail of the energy distribution now extending past 15 eV. The few-cycle data, in particular the significant enhancement of energy with which H^+ fragments are formed in few-cycle measurements compared to those made with 100-fs pulses, are a manifestation of nonadiabatic effects and are a corollary to what has been observed in earlier studies of HHG.

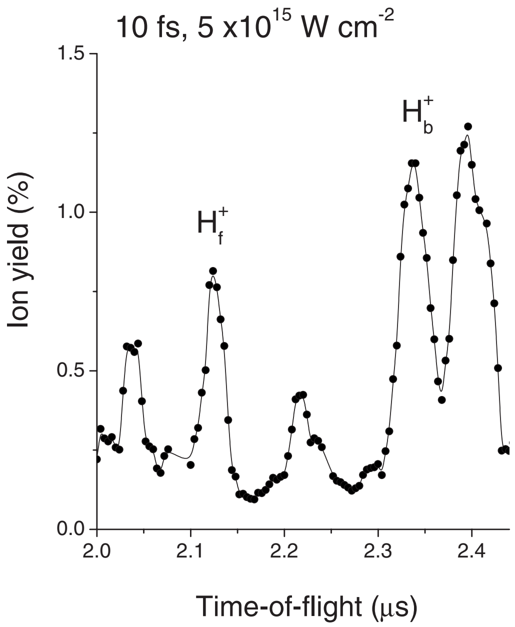

FIG. 5. High-resolution TOF spectrum showing H^+ fragments obtained upon irradiation of H_2O with 10-fs pulses. The spectrum has been normalized to the H_2O^+ peak.

In discussing nonadiabaticity it is important to take cognizance of the energy transfer from the ultrashort optical field to the water molecule. We estimate the efficiency of energy transfer by invoking the Massey criterion [21], which has had a long history of successful application in atomic collision physics. The Massey criterion qualitatively defines an adiabatic parameter, $\lambda_M = \tau_c / \tau_v$, by comparing the duration of the interaction, τ_c, with the period of O-H vibration in the water molecule, τ_v. When $\lambda_M \ll 1$, the interaction is considered to be "sudden" and energy transfer is efficient. For

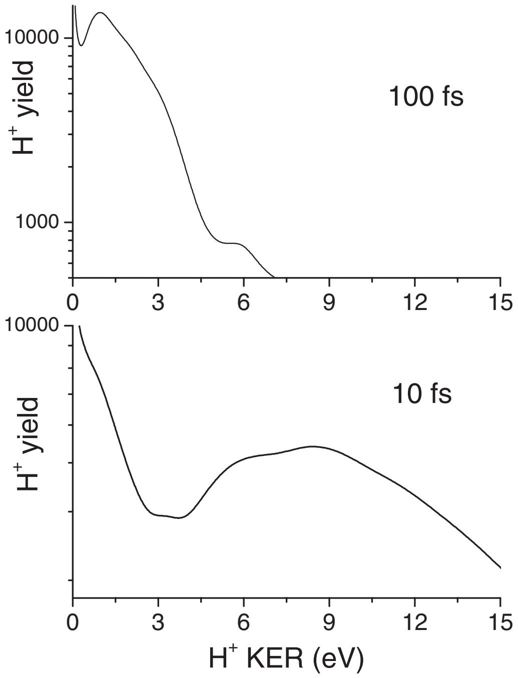

FIG. 6. Distribution of kinetic energies of H^+ fragments produced upon irradiation of water by 100-fs (top panel) and 10-fs (bottom panel) pulses.

$\lambda_M \gg 1$, one obtains the adiabatic limit where energy transfer becomes inefficient. In the context of energy transfer from a pulsed optical field to H_2O, the Massey criterion has to be modified to account for the pulse duration and the magnitude of the optical field with respect to E_a, the field required to suppress the Coulomb barrier to the level of the ionization energy, V_{ion}. Augst and co-workers [22] have established that $E_a = V_{ion}^2/4$. In the context of HHG in atoms, calculations [9] have shown that for $E \ll E_a$, HHG is unaffected by pulse duration. For strong fields $(E \sim E_a)$ of ultrashort duration, the irradiated atom is exposed to higher field strengths, as already noted above. This implies that larger amounts of kinetic energy are gained by the ionized electron, which, in turn, gives rise to more energetic and more intense harmonics in the HHG spectrum. In our experiment, the intensity values were well in the 10^{15} W cm^{-2} range, and $E \sim E_a$, ensuring that our operating conditions were away from the adiabatic regime as far as the H_2O molecule is concerned. This nonadiabaticity gives rise to the ionized electron (or electrons) being exposed to higher amplitudes of the applied field, resulting in "hotter" electrons, which, upon recollision with the molecular core, result in further ionization to $H_2O^{q+\star}$ $(q>2)$ states that are electronically excited. Subsequent dissociation of such highly excited $H_2O^{q+\star}$ states gives rise to protons that are more energetic than would be the case if protons are generated upon dissociation of lower-energy states of H_2O^{q+}. We note from results of quantum chemical studies of multiple-charged molecular states of diatomic molecules [23] that higher degrees of electronic excitation result in larger kinetic energy releases, asymptotically converging on the Coulomb repulsion energy. In recent experiments conducted on CS_2 molecules [4], observation of CS_2^{2+} and CS_2^{3+} in the few-cycle regime are consistent with our nonadiabatic picture of the ultrafast dynamics. While CS_2^{2+} and CS_2^{3+} are both long lived [24], it is known that the corresponding dication and trication states of water are too short lived to be directly detected in mass spectra [25]. The energetic protons that we observe are signatures that such states are being populated in our few-cycle experiments.

Apart from demonstrating the advent of nonadiabatic dynamics in the few-cycle ionization of water, what are the other implications of the proton energy spectra that we have measured? Recent work on H_2 and D_2 molecules has established that it is convenient to characterize strong-field dynamics in terms of sequential and recollision ionization. The former occurs predominantly when H_2 is irradiated at laser intensities below $\sim 10^{14}$ W cm^{-2} while the latter dominates at higher intensity values [3,5,18,26]. The important strong-field process of enhanced ionization plays an effective role in sequential ionization but, as already discussed above, is of little or no consequence in the few-cycle domain. So what bearing does our few-cycle energy spectrum have on the question of how the strong-field dynamics proceeds in the case of water? If sequential ionization were to dominate, consideration of the time delay between the field-induced ejection of the first and second electrons would be expected to manifest itself in the energy spectrum in the following manner. After ejection of the first electron, giving rise to the formation of the H_2O^+ parent molecular ion, a nuclear wave packet would be launched due to the nonlinear and nonresonant coupling between the $^2B_1$ lowest-energy state of H_2O^+ and the appropriate dissociative electronic state of the molecular ion. It is during the evolution of this nuclear wave packet and the accompanying lengthening of the O-H bonds that the second electron would be field ionized (we note that the vibrational time period for the O-H bond is ~ 9 fs [27]). The longer O-H bond at which double ionization occurs would give rise to a H^+ fragment kinetic energy that would be less than that which would result if instantaneous nonsequential ejection of two electrons were to occur. In other words, the energy spectrum for the sequential ionization process would exhibit lower-energy features than in the case of recollision ionization. Our results for water indicate that recollisions give rise to energetic proton formation when intense 10-fs pulses are used to irradiate water molecules at intensity levels in the 10^{15} W cm^{-2} range and higher.

Further insight into the dynamics emerges when experiments are carried out in which the polarization properties of the incident light are modified. Figure 4 shows how the H^+ TOF spectrum alters when the polarization state is altered from linear to circular, adjusting the intensity such that the magnitude of the optical field that irradiates the water molecules is kept constant. Energetic H^+ fragments are now almost totally eliminated; indeed, at the intensity value pertinent to the spectrum shown in Fig. 4, the proton signal itself almost totally disappears. This provides us with direct and unambiguous evidence that H^+ formation is almost exclusively due to electron recollision. It is of interest to note that recent experiments on electron and ion yields from polyatomic molecules have yielded evidence that quantal effects, notably electronic structure effects in molecules, can affect the role that rescattering plays in strong-field molecular dynamics [4,28]. We note that in strong-field double ionization of H_2 [5] induced by $\sim$15-fs pulses, it was found that the first return recollision essentially dominates the rescattering dynamics, whereas for longer pulses, the third return recollision assumes importance. Experiments on methane [2] also highlighted the importance of the first return recollision when 8-fs pulses were used: no dications were observed with such ultrashort pulses, but they began to appear when longer pulses were used. In recent work on CS_2 [4], it was found that dication and trication parent ions were formed by sequential ionization and dominated the spectrum obtained using four-cycle pulses, ostensibly at the expense of fragmentation channels. In these experiments rescattering was "switched off" not because of temporal constraints but those imposed by the quantal properties associated with the outermost $2\pi_g$ orbital of CS_2: the wave packet of the returning electron interferes destructively with the large spatial extent of this orbital, leading to effective cancellation of the rescattering process. Thus, the returning electron's energy is no longer available for electronic excitation to CS_2^{+*} states that are quantally allowed to dissociate into $S^+ + CS$ or $S + CS^+$. Clearly, the nonbonding $1b_1$ outermost orbital in water plays no such role: rescattering is not nullified and is an ultrafast process that continues to have an important role to play in the strong-field dissociative ionization of water in both the 100-fs and 10-fs temporal domains.

In summary, we have demonstrated the use of four-cycle pulses of intense 800-nm light to ionize and dissociate water molecules in the intensity and temporal regime where recollision ionization dominates the laser-molecule interaction and processes like enhanced ionization and spatial alignment are “switched off.” Nonadiabatic effects drive the overall dynamics in the few-cycle regime, giving rise to single and multiple molecular ionization to higher excited states of H_2O^{q+}, $q \geqslant 2$. The experimental manifestation of nonadiabatic processes affecting the dynamics is in significantly higher amounts of kinetic energy being released upon dissociation of water into atomic fragments. The energy spectrum of H^+ fragments also enables us to deduce that recollision nonsequential ionization drives the overall dynamics.

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